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(54) Abstract Title

Ink jet ink composition

(57) An ink having a viscosity less than 20cp at 20°C comprising (i) a coloured polymer obtained by colouration of a polymer having anhydride groups and (ii) a liquid medium. The polymer is obtained from the polymerisation of maleic anhydride monomers and the liquid medium comprises water and an organic solvent. The ink is suitable for use in jet printing.

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INK-JET INK COMPOSITION

This invention relates to inks comprising coloured polymers and to their use in ink jet printing.

Ink jet printing methods involve a non-impact printing technique for printing an image onto a substrate using ink droplets ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for colorants and inks used in ink jet printing. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle. The most popular ink jet printers are thermal and piezoelectric ink jet printers.

There is a need for inks which are suitable for both thermal and piezo ink jet printers, have high colour strength and produce images having a high light-fastness and water-fastness when printed on a substrate.

We have found that coloured polymers obtainable by the coloration of a polymer carrying anhydride groups are suitable for use in inks for thermal and piezo ink jet printers.

According to the present invention there is provided an ink having a viscosity less than 20 cp at 20°C, comprising the components:

- (a) a coloured polymer obtainable by the coloration of a polymer carrying anhydride groups; and
- (b) a liquid medium.

The coloration of a polymer carrying anhydride groups preferably comprises the formation of a covalent bond between the polymer and a colorant.

Alternatively coloration of the polymer carrying anhydride groups comprises reaction of the anhydride groups with a colorant precursor thereby forming a covalent bond therebetween and subsequently converting the colorant precursor to a colorant.

If a bridging compound carrying a nucleophilic group is employed coloration of the polymer carrying anhydride groups comprises reaction of the anhydride groups with a bridging compound thereby forming a covalent bond therebetween and subsequently reacting the bridging group with a colorant or colorant precursor.

Preferably the colorant, colorant precursor and bridging compound carry at least a nucleophilic group(s) capable of reacting with the polymer carrying anhydride groups.

When the anhydride group reacts with the nucleophilic group(s) carried by the colorant, bridging compound or colorant precursor a ring opening reaction occurs resulting in the formation of a covalent bond between the polymer and colorant, bridging compound or colorant precursor and the formation of a pendant carboxylic acid moiety.

5 The carboxylic acid group, when neutralised may act as a water-dispersing group.

The process for the formation of coloured polymer preferably comprises the reaction of the nucleophilic group(s) carried by the colorant, colorant precursor or bridging compound with the polymer carrying anhydride groups at a temperature of from 10°C to 130°C, more preferably 15°C to 100°C. The reaction is usually continued until

10 the reaction between components is substantially complete.

The reaction may be performed in a solvent or as a melt of the components. Preferably the reaction is performed under anhydrous conditions. If the reaction is performed in a solvent, preferably an organic solvent is used. The colorant, colorant precursor or bridging compound may be added to a solution of the polymer carrying

15 anhydride groups or the polymer carrying anhydride groups may be added to a solution of the colorant, colorant precursor or bridging compound.

The colorant, colorant precursor or bridging compound is preferably soluble in the solvent used for the reaction. If the colorant is not soluble in the solvent then the colorant can be reacted with the polymer carrying anhydride groups via bridging

20 compounds which are soluble in the solvent. The amount of colorant used normally depends on the amount of coloration desired. Any excess anhydride groups left after reaction with the colorant may be hydrolysed, if desired, to give the diacid or diacid salts. The relative amounts of the polymer carrying anhydride groups and the colorant are preferably selected such that the mole ratio of colorant to anhydride groups is from 1:20

25 to 10:1. The relative amount is more preferably selected such that the mole ratio of colorant to anhydride groups is from 1:4 to 2:1, especially from 3:10 to 1:1:1.

If desired a catalyst may be used in the reaction to assist formation of the coloured polymers. Suitable catalysts include non-nucleophilic bases, for example Et_3N , NaOBu^+ , 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) 4-dimethylaminopyridine (DMAP),

30 1,4-Diazabicyclo[2.2.2]octane (DABCO) and K_2CO_3 .

An organic solvent may optionally be included in the reaction mixture to lower the viscosity of the reaction mixture. Preferably water-miscible organic solvents are used, for example N,N-dimethylformamide, N-methylpyrrolidone, dimethyl sulphoxide, dialkyl ethers of glycol acetates or mixtures thereof are used.

35 The process for the formation of the coloured polymer may further comprise a step where a dispersant is reacted with the resultant coloured polymer.

The coloured polymer is preferably soluble in water, although minor amounts of the coloured polymer may be insoluble in water and exist as dispersed particles when mixed with aqueous media or water.

40 The coloured polymer may be purified if desired in the usual way for colorants used in ink jet printing inks. For example a mixture of the coloured polymer and water

may be purified by ion-exchange, filtration, reverse osmosis, dialysis, ultra-filtration or a combination thereof. In this way one may remove co-solvents used during the preparation of the coloured polymer, low molecular weight salts, impurities and free monomers.

5 Preferably the colorant has one nucleophilic group capable of reacting with the anhydride groups on the polymer carrying anhydride groups. Colorants having two nucleophilic groups may be present in low levels, preferably not exceeding 5% by weight relative to the total weight of the colorant. If a colorant has several nucleophilic groups, preferably one of the nucleophilic groups has a higher reactivity than the other(s)
10 resulting in only one of the nucleophilic groups reacting with the anhydride group, thus minimising crosslinking.

Examples of suitable nucleophilic group(s) include, but are not limited to, alcohols, primary amines, secondary amines and thiols. The nucleophilic group(s) may be attached directly to the colorant or through a bridging compound. A bridging
15 compound has at least one nucleophilic group that can react with the anhydride group on the polymer carrying anhydride groups and at least one functional group that can react with a colorant or colorant precursor. The bridging compound may be a di-, tri-, tetra- or polyfunctional structure, and examples include, but are not limited to bis alkyl halides, tris dialkyl halides, bis acid chlorides, tris diacid chlorides, cyanuric chloride and
20 related reactive 1,3,5-triazines, other reactive heterocyclic halides and aromatic halides. An example of a suitable bridging compound is an alkyldiamine attached to the colorant via a triazine ring.

The colorant preferably comprises from 1 to 10, more preferably 1 to 5, especially 1, 2 or 3 colorants having at least one nucleophilic group capable of reacting
25 with the polymer carrying anhydride groups. The colorant preferably comprises a chromophore.

The chromophore preferably comprises an azo, heterocyclic azo, anthraquinone, pyrroline, phthalocyanine, polymethine, aryl-carbonium, triphenodioxazine, benzodifuranone, or indolene chromophoric group or a combination thereof. Preferred
30 chromophores are azo chromophoric groups, especially monoazo, disazo, trisazo, heterocyclic azo and phthalocyanine chromophoric groups. For example the colorant may be a chromophore such as an azo group which is reacted directly with the polymer carrying anhydride groups.

Alternatively a colorant precursor such as an azo group precursor may be used
35 which is reacted directly with the polymer carrying anhydride groups followed by conversion of the azo group precursor to the azo group in a separate diazotisation reaction. The diazotisation reaction comprises the steps:

- (i) diazotising an amino group in a colourless compound using a diazotising agent;
and
- 40 (ii) coupling the product of step (i) with a coupling component forming an azo group therebetween, resulting in a coloured compound.

The colorant is preferably a dye, more preferably a dye which is soluble in organic solvents or in water, especially in water. Water solubility may be achieved by the presence of water-dispersing groups as hereinbefore described in the dye. Preferably acidic groups are present in the dye. Preferred acidic groups are phosphonic, carboxylic or sulphonic acids, and combinations and salts thereof. Solubility in an organic solvent may be increased by changing the salt counter ion to increase organic solubility, for example from Na^+ to $n\text{-butyl}_3\text{N}^+\text{H}$.

The carboxylic and sulphonic acid groups may be subsequently fully or partially neutralised with a base containing a cationic charge to give a salt. If the carboxylic or sulphonic acid groups are used in combination with a non-ionic water-dispersing group, neutralisation may not be required. The conversion of any free acid groups into the corresponding salt may be effected during the preparation of the coloured polymer and/or during the preparation of an ink from the coloured polymer.

Preferably the base used to neutralise any acid dispersing groups is ammonia, an amine or an inorganic base. Suitable amines are tertiary amines, for example triethylamine or triethanolamine. Suitable inorganic bases include alkaline hydroxides and carbonates, for example lithium hydroxide, sodium hydroxide, or potassium hydroxide. A quaternary ammonium hydroxide, for example $\text{N}^+(\text{CH}_3)_4\text{OH}^-$, can also be used. Generally a base is used which gives the required counter ion desired for the ink which is prepared from the coloured polymer. For example, suitable counter ions include Li^+ , Na^+ , K^+ , NH_4^+ and substituted ammonium salts. NH_4^+ is especially preferred.

Preferably the polymer carrying anhydride groups is a copolymer, for example an alternating, block or random copolymer, preferably an alternating copolymer.

Preferably the polymer carrying anhydride groups has a weight average molecular weight (Mw) less than 70,000. This is because a lower molecular weight leads to an improved performance of inks containing the coloured polymer, especially for use in thermal ink jet printers. The Mw is preferably less than 60,000, more preferably less than 50,000.

Mw may be measured by gel permeation chromatography. The gel permeation chromatography method used for determining Mw preferably comprises applying the uncoloured polymer carrying anhydride groups to a chromatography column packed with cross-linked polystyrene/divinyl benzene, eluting the column with tetrahydrofuran at a temperature of 40°C and assessing the Mw of the polymer carrying anhydride groups compared to a number of polystyrene standards of a known Mw. Suitable chromatography columns packed with cross-linked polystyrene/divinyl benzene are commercially available from Polymer Laboratories.

An alternative method for measuring Mw of the polymer carrying anhydride groups includes for example multi angle light scattering.

The copolymer has preferably been obtained from the polymerisation of one or more olefinically unsaturated monomers having anhydride groups and one more olefinically unsaturated monomers which are free from anhydride groups.

Preferred olefinically unsaturated monomers having anhydride groups include but are not limited to itaconic anhydride, maleic anhydride, dimethylmaleic anhydride, bromomaleic anhydride, chloromaleic anhydride, and dichloromaleic anhydride, especially preferred is maleic anhydride.

5 Olefinically unsaturated monomers free from anhydride groups include olefinically unsaturated monomers having water-dispersing groups and olefinically unsaturated monomers free from water-dispersing groups.

Water-dispersing groups provide the facility of self-dispersibility and solubility to the coloured polymer in ink media, especially in water. The nature and level of water-dispersing groups influences whether a solution, dispersion emulsion or suspension is
10 formed in the ink media. The level of water-dispersing groups may vary but is preferably sufficient to form stable inks in ink media. Preferably the coloured polymer is water-dissipatable. The water-dispersing groups may be ionic, non-ionic or a mixture of ionic and non-ionic water-dispersing groups. Preferred ionic water-dispersing groups include
15 basic amine groups, cationic quaternary ammonium groups and acid groups, for example phosphoric acid groups, sulphonic acid groups and carboxylic acid groups.

The acid groups may be subsequently fully or partially neutralised with a base containing a cationic charge to give a salt. If the acid groups are used in combination with a non-ionic water-dispersing group, neutralisation may not be required. The
20 conversion of any free acid groups into the corresponding salt may be effected during the preparation of the coloured polymer and/or during the preparation of an ink from the coloured polymer.

Preferably the base used to neutralise any acid groups is ammonia, an amine or an inorganic base. Suitable amines are tertiary amines, for example triethylamine or triethanolamine. Suitable inorganic bases include alkaline hydroxides and carbonates,
25 for example lithium hydroxide, sodium hydroxide, or potassium hydroxide. A quaternary ammonium hydroxide, for example $N^+(CH_3)_4OH^-$, can also be used. Generally a base is used which gives the required counter ion desired for the ink which is prepared from the coloured polymer. For example, suitable counter ions include Li^+ , Na^+ , K^+ , NH_4^+ and
30 substituted ammonium salts.

Preferred olefinically unsaturated monomers providing ionic water-dispersing groups include acrylic acid, methacrylic acid, itaconic acid, maleic acid, monoalkyl itaconates, citraconic acid, styrenesulfonic acid, vinylbenzylsulfonic acid, vinylsulfonic acid, acryloyloxyalkyl sulfonic acids 2-acrylamido-2-alkylalkane sulfonic acids, 2-
35 methacrylamido-2-alkylalkane sulfonic acids, mono-(acryloyloxyalkyl)phosphates and mono(methacryloyloxyalkyl)phosphates.

Preferably non-ionic water-dispersing groups are pendant polyoxyalkylene groups, more preferably polyoxyethylene groups.

Preferred olefinically unsaturated monomers providing non-ionic water-dispersing
40 groups include alkoxy polyethylene glycol (meth)acrylates, preferably having a number average molecular weight of from 350 to 2000. Examples of such monomers which are

commercially available include ω -methoxypolyethylene glycol acrylate and diethylene glycol vinyl ether.

Preferred olefinically unsaturated monomers which are free from water-dispersing groups include alkyl(meth)acrylates, optionally substituted styrenes, methacrylamides, allyl compounds, dienes, vinyl ethers, vinyl ketones, vinyl esters, vinyl amides, vinyl furans, vinyl halides, vinylidene halides, olefins and unsaturated nitriles.

Preferred alkyl(meth)acrylates contain less than twenty carbon atoms. Examples include methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl, sec-butyl acrylate, amyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, tert-octyl acrylate, 2-phenoxyethyl acrylate, 2-chloroethyl acrylate, 2-bromoethyl acrylate, 4-chlorobutyl acrylate, cyanoethyl acrylate, 2-acetoxyethyl acrylate, dimethylaminoethyl acrylate, benzyl acrylate, methoxybenzyl acrylate, 2-chlorocyclohexyl acrylate, acrylate, cyclohexyl acrylate, furfuryl acrylate, tetrahydrofurfuryl acrylate, phenyl acrylate, 5-hydroxypentyl acrylate, 2,2-dimethyl-3-hydroxypropyl acrylate, 2-methoxyethyl acrylate, 3-methoxybutyl acrylate, 2-ethoxyethyl acrylate, 2-isopropoxyethyl acrylate, 2-butoxyethyl acrylate, 2-(2-methoxyethoxy)ethyl acrylate, 2-(2-butoxyethoxy)ethyl acrylate, 1-bromo-2-methoxyethyl acrylate, 1,1-dichloro-2-ethoxyethyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, sec-butyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzylmethacrylate, chlorobenzyl methacrylate, octyl methacrylate, N-ethyl-N-phenylaminoethyl methacrylate, 2-(3-phenylpropyloxy)ethyl methacrylate, dimethylaminophenoxyethyl methacrylate and furfuryl methacrylate.

Preferred optionally substituted styrenes include styrene, methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, diethylstyrene, isopropylstyrene, butylstyrene, hexylstyrene, cyclohexylstyrene, decylstyrene, chloromethylstyrene, trifluoromethylstyrene, ethoxymethylstyrene, acetoxymethylstyrene, methoxystyrene, 4-methoxy-3-methylstyrene, dimethoxystyrene, chlorostyrene, dichlorostyrene, trichlorostyrene, tetrachlorostyrene, pentachlorostyrene, bromostyrene, dibromostyrene, iodostyrene, trifluorostyrene and 2-bromo-4-trifluoromethylstyrene.

Preferred methacrylamides contain less than 12 carbon atoms. Examples include methylmethacrylamide, tert-butylmethacrylamide, tert-octylmethacrylamide, benzylmethacrylamide, cyclohexylmethacrylamide, phenylmethacrylamide, dimethylmethacrylamide, dipropylmethacrylamide, hydroxyethyl-N-methylmethacrylamide, N-methylphenylmethacrylamide, N-ethyl-N-phenylmethacrylamide and methacrylhydrazine.

Preferred vinyl ethers contain less than 20 carbon atoms. Examples include methyl vinyl ether, butyl vinyl ether, hexyl vinyl ether, octyl vinyl ether, decyl vinyl ether, ethylhexyl vinyl ether, methoxyethyl vinyl ether, ethoxyethyl vinyl ether, chloroethyl vinyl ether, 1-methyl-2,2-dimethylpropyl vinyl ether, 2-ethylbutyl vinyl ether, hydroxyethyl vinyl ether and dimethylaminoethyl vinyl ether.

Preferred vinyl ketones contain less than 12 carbon atoms. Examples include methyl vinyl ketone, phenyl vinyl ketone and methoxyethyl vinyl ketone.

Preferred vinyl halides include vinyl chloride, vinylidene chloride and chlorotrifluoro ethylene.

5 Preferred unsaturated nitriles include acrylonitrile and methacrylonitrile

The polymer carrying anhydride groups may be prepared in a conventional manner by polymerising the olefinically unsaturated monomers having anhydride groups and olefinically unsaturated monomers free from anhydride groups.

10 Preferred polymerisation methods include solution polymerisation, emulsion polymerisation, suspension polymerisation and solution/dispersion polymerisation and such general methods as are well known in the art. More preferably aqueous or non-aqueous solution polymerisation and emulsion polymerisation is used and most preferably solution polymerisation is used. Temperatures of from 20°C and 180°C are preferred. The polymerisation may be continued until reaction between the monomers

15 is complete.

If desired, an initiator may be used to assist polymerisation. Suitable initiators are free-radical generators. Examples of catalysts include azobis compounds, peroxides, hydroperoxides, redox catalysts, etc., for example, potassium persulfate, ammonium persulfate, tert-butyl peroctoate, benzoyl peroxide, isopropyl percarbonate,

20 2,4-dichlorobenzoyl peroxide, methyl ethyl ketone peroxide, cumene hydroperoxide, dicumyl peroxide, azobisisobutyronitrile, azobis(2-amidino-propane)hydrochloride and the like.

Typically 0.05 to 5% by weight of initiator is used relative to the total weight of the olefinically unsaturated monomers. Preferably the polymerisation is performed in

25 the presence of an emulsifying agent.

The Mw of the polymer carrying anhydride groups may be controlled by the addition of chain transfer agents and/or through the adjustment of the ratio of the concentration of olefinically unsaturated monomers relative to the concentration of initiator during the course of the polymerisation. Typical chain transfer agents are thiols,

30 halocarbons and cobalt macrocycles.

Maleic anhydride monomer for example can be used in addition and condensation type polymerisation as well as be homopolymerised with γ - and uv radiation, in the presence of radical initiators and anionically with various bases. Maleic anhydride monomer is easily copolymerised with olefinically unsaturated comonomers.

35 The maleic anhydride functionality on the polymer backbone promotes or improves hydrophilicity. A description of these polymers and how to make them can be found in 'Encyclopaedia of Polymer Scienc and Engineering' Vol. 9: page 225, Maleic and Fumaric Polymers and Vol. 4: page 233, Copolym rs, Alternating.

Preferably the polymer carrying anhydride groups is free from aromatic groups. It

40 is also preferred that the polymer carrying anhydride groups is free from olefinic ($>C=C<$ carbon-carbon double bonds) groups. Any residual olefinic groups (from for

example the copolymerisation of butadiene with maleic anhydride) may be removed by hydrogenation with a suitable catalyst. Suitable hydrogenation techniques include reaction of the ethylen group with hydrogen in the presence of a catalyst as known in the art, for example palladium or platinum on carbon catalysts

5 The absence of aromatic groups and carbon-carbon double bonds in the polymer carrying anhydride groups have been found to improve light fastness properties of the ink.

Preferably the ink according to the present invention comprises:
from 0.25 to 30 parts of component (a) (the coloured polymer) and from 70 to 99.75
10 parts of component (b) (the liquid medium), wherein all parts are by weight and the number of parts of (a) + (b) = 100.

The number of parts of the coloured polymer are preferably from 0.5 to 28, more preferably from 2 to 25, and especially from 2.5 to 20 parts of the coloured polymer and from 70 to 99.75 parts of the liquid medium wherein all parts are by weight and the
15 number of parts add up to 100.

The inks according to the present invention may be prepared by mixing the coloured polymer with a liquid medium. Suitable techniques are well known in the art, for example agitation, ultrasonication or stirring of the mixture. The mixture of coloured polymer and liquid medium may be in the form of a dispersion, emulsification,
20 suspension, solution or mixture thereof.

Preferably the coloured polymer is mixed with a first liquid medium, followed by mixing the resultant mixture with a second liquid medium.

The liquid medium is preferably water, a mixture of water and an organic solvent or an organic solvent free from water. For example the coloured polymer may be added
25 to water followed by the addition of one or more organic solvents. Preferably the first liquid medium is an organic solvent and the second liquid medium is water and a mixture of water and one or more organic solvents.

When the liquid medium comprises a mixture of water and an organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably
30 from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide;
35 ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol
40 and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and

1,2,6-hexanetriol; mono-C₁₋₄-alkyl ethers of diols, preferably mono-C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulphoxides, preferably dimethyl sulfoxide and sulpholane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-soluble organic solvents.

Especially preferred water-soluble organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono-C₁₋₄-alkyl and C₁₋₄-alkyl ethers of diols, more preferably mono-C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH₂Cl₂; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the dye in the liquid medium. Examples of polar solvents include C₁₋₄-alcohols. In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) and or an alcohol (especially a C₁₋₄-alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected which gives good control over the drying characteristics and storage stability of the ink.

Inks comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

A preferred liquid medium comprises:

- (i) from 75 to 95 parts water; and
- (ii) from 25 to 5 parts in total of one or more solvents selected from diethylene glycol, 2-pyrrolidone, thiodiglycol, N-methylpyrrolidone, cyclohexanol, caprolactone, caprolactam and pentane-1,5-diol;

wherein the parts are by weight and the sum of the parts (i) and (ii) = 100.

The ink may also contain a surfactant. This helps to dissipate the coloured polymer in addition to the dissipation caused by the optional water-dispersing groups contained in the coloured polymer.

5 The ink preferably has a pH of from 6 to 11, more preferably of from 7 to 10. Such a pH may be obtained by the addition of a base or a pH buffer. Where a base or buffer is used this may be any suitable base or buffer, and may preferably be the same base as was used to neutralise any anionic dispersing groups during the preparation of the coloured polymer.

10 The viscosity of the ink is preferably less than 20cp, more preferably less than 15cp, especially less than 10cp at 20°C.

The inks of the present invention have the advantage that they are suitable for piezoelectric, thermal and continuous ink jet printers. Many other inks based on water-dissipatable polymers work poorly or even not at all in thermal ink jet printers.

15 Inks of the invention form discrete droplets on the substrate with little tendency for diffusing. Consequently sharp images with excellent print quality and little if any bleed between colours printed side by side can be obtained. Furthermore the inks show good storage stability, wet and light fastness and fastness to both acidic and alkaline highlighter pens.

20 A further aspect of the invention provides a process for printing an image on a substrate comprising applying thereto an ink of the present invention by means of an ink jet printer.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small nozzle onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the nozzle, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the nozzle. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the nozzle.

30 The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain, coated or treated papers which may have an acid, alkaline or neutral character. Most preferably the substrate is a plain or coated paper.

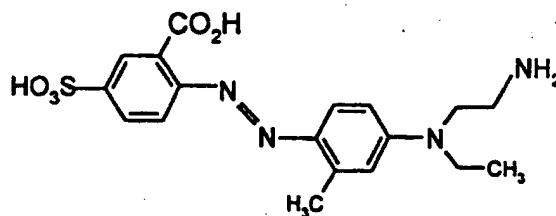
35 According to a further feature of the invention there is provided an ink jet printer cartridge optionally a refillable ink jet printer cartridge containing an ink as hereinbefore defined.

The invention will now be described by example only. All parts and percentages are by weight unless specified otherwise.

40

Colorant 1:

A colorant of Formula 1 was prepared as follows:



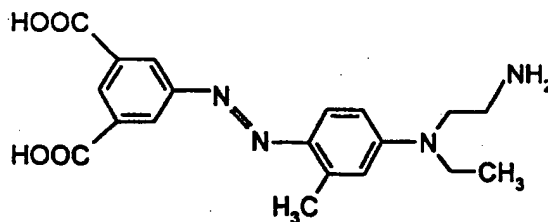
Formula 1

A stirred mixture of 5-sulphoanthranilic acid (10.8g), water (500cm³) and concentrated hydrochloric acid (30cm³) was cooled to 0-5°C. 2N Sodium nitrite solution (30cm³) was added dropwise. This mixture was stirred for a further 1 hour at 0-5°C and then an excess of 10% aqueous sulphamic acid was added to destroy any excess nitrous acid.

The resultant mixture was then added to a stirred, cooled (0-5°C) mixture of N-ethyl-N-β-aminoethyl-m-toluidine (8.9g) in a mixture of acetone (500 cm³) and water (500 cm³) while maintaining the pH at around 5 by the addition of sodium acetate solution. The stirred mixture was then allowed to warm up to room temperature and stirred for 18 hours. The product was isolated by filtration, washed with cold water and dried in an oven at approximately 70°C to yield 21g of the colorant of Formula 1.

Colorant 2:

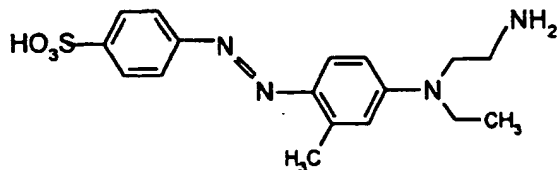
A colorant of Formula 2 was prepared in the same manner as colorant 1 except that 5-amminoisophthalic acid (8.6g) was used instead of 5-sulphoanthranilic acid.



Formula 2

Colorant 3:

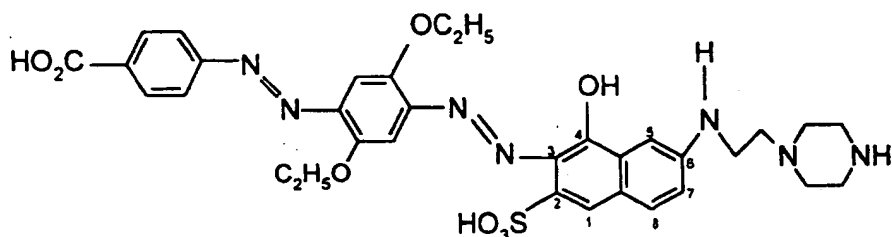
A colorant of Formula 3 was prepared in same manner as colorant 1 except that sulphanilic acid (9.0g) was used instead of 5-sulphoanthranilic acid.



Formula 3

Colorant 4:

A colorant of Formula 4 was prepared as follows:



Formula 4

Stage 1

4-Amino benzoic acid (217.43g, ex Aldrich) was dissolved in a solution of water (400cm³) at containing pH 8.5 sodium nitrite (16.56g, 0.24M). The solution was filtered to remove any insoluble material.

Concentrated hydrochloric acid (75cm³) was stirred into ice/water (400cm³) at < 5°C and the above solution was added dropwise over 30 minutes. The mixture was stirred at < 5°C for 2 hours after which any excess nitrous acid was destroyed by addition of sulphamic acid.

2,5-Diethoxy aniline (36.25g, ex TCI-Japan) was dissolved in ethanol (700cm³) and added to the above mixture at < 5°C to give an orange suspension of a monoazo product. The product was filtered off, washed with water and dried at 70°C.

Stage 2

The product from Stage 1 (1.69g) was stirred in water (25cm³) and 46/48% sodium hydroxide solution (1.5cm³) was added to give an orange solution.

A mixture of hydrochloric acid, specific gravity 1.18 (3cm³) in water (50cm³) was cooled to 0-5°C and stirred rapidly. The orange solution was added dropwise and the resulting diazonium mixture allowed to warm to ambient temperature after which any excess nitrous acid was destroyed by addition of 10% sulphamic acid solution.

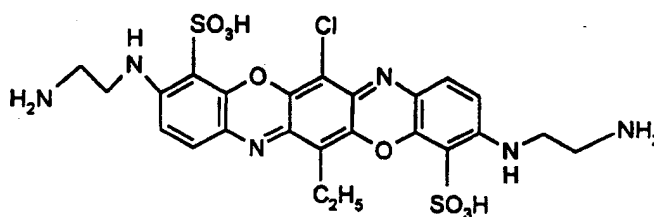
A piperazine-gamma acid derivative [6-(N-ethyl piperazonyl)amino-4-hydroxy-2-naphthalene sulphonic acid] (1.59g) was stirred in water (50cm³) and adjusted to pH

11.0 by addition of 48% sodium hydroxide solution. The mixture was cooled to 0-5°C and the above diazonium mixture was added dropwise and stirred for 18 hours at 0-5°C. The resulting solution was adjusted to pH 2 by addition of hydrochloric acid and sodium chloride was added to give a dark precipitate which was filtered and dried. The precipitate was dissolved in aqueous ammonia, precipitated by acidification with hydrochloric acid, isolated by filtration and washed with distilled water. The dissolving, isolation and precipitation process was then repeated.

The resultant solid was dissolved in aqueous ammonia and filtered through a cascade of filters (Glass microfibre GF/A, GF/F and membrane) to 0.45 micron and then purified by reverse osmosis using "Visqueen" tubing and the resulting solution dried at 50°C to give a colorant of Formula 4.

Colorant 5

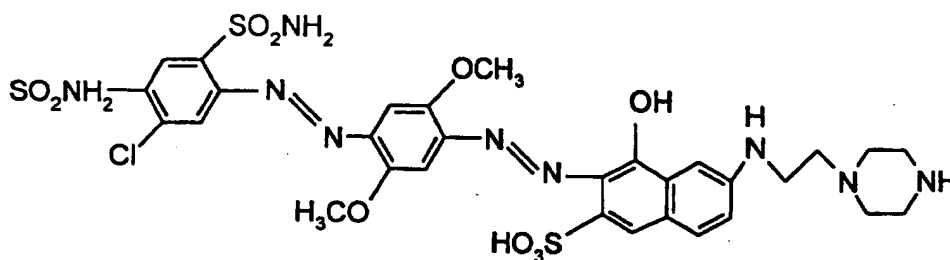
A colorant of Formula 5 was prepared as described in EP 576123A1, Example 1 stages a to c incorporated herein by reference.



Formula 5

Colorant 6:

A colorant of Formula 6 was prepared as follows:



Formula 6

Stage 1

4-Amino-6-chloro-1,3-benzenedisulphonamide (28.6g, ex Aldrich) was dissolved in a mixture of water (500cm³) at pH 13 and sodium nitrite (7.0g). The solution was added dropwise to a stirred mixture of hydrochloric acid, specific gravity 1.18 (60cm³) and water (500cm³) at 0.5°C. The mixture was stirred for 2 hours after which any excess nitrous acid was destroyed by addition of sulphamic acid.

2,5-dimethoxy aniline (18g, x Aldrich) was dissolved in a mixture of methanol (200 cm³) and water (400cm³) and cooled to 0-5°C and added to the above mixture giving an orange suspension which was stirred for 18 hours. The orange suspension was adjusted to pH 4 by addition of sodium acetate, filtered, washed with water and dried at 70°C to give a monoazo product.

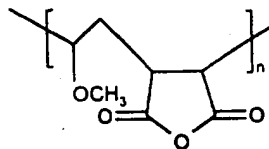
Stage 2

The monoazo product from stage 1 was stirred in water (400cm³) at pH 9-10 and 2N sodium nitrite solution (65cm³) was added to give a suspension. A mixture of hydrochloric acid, specific gravity 1.18 (70cm³) and water (600cm³) was stirred rapidly, the suspension was added at 0-5 °C and stirred at room temperature for 1 hour to give a diazo product after which sulphamic acid was added to destroy any excess nitrous acid.

6(-N-ethyl piperazeryl) amino-4-hydroxy-2-naphthalene sulphonic acid (12.8g, was dissolved in water (600cm³) at pH 10 and cooled to 0-5°C. The above diazo product was added dropwise, maintaining the mixture at pH 10 and 0-5°C throughout the addition. The mixture was stirred at room temperature for 18 hours, adjusted to pH 2-3 by addition of hydrochloric acid, specific gravity 1.18 and sodium chloride was added to yield a dark solid which was filtered, washed with acetone and dried to give a colorant of Formula 6.

Coloured Polymer 1

A coloured polymer was prepared from a polymer carrying anhydride groups having repeat units of Formula 7 and a colorant of Formula 1 as described below.



Formula 7

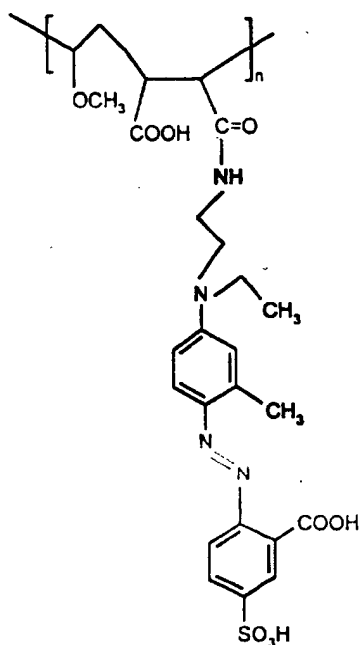
Step 1) Preparation of the coloured polymer:

A mixture of a polymer carrying anhydride groups [poly(vinyl methyl ether/maleic anhydride) (1:1 molar) (CAS no. 9011-16-9, Mn 41000, Polysciences Inc) (1.56g), the colorant of Formula 1 (4.0g), potassium carbonate (1.0g) and N,N-dimethylformamide (DMF) (50g) was stirred at 70°C for 18 hours. A further addition of the poly(vinyl methyl ether/maleic anhydride) (1.56g) was made together with triethylamine (1.0g) and the mixture was stirred at 70°C for 72 hours. The mixture was cooled to room temperature and added slowly to a stirred mixture of concentrated hydrochloric acid (5cm³) and distilled water (200cm³). The resultant tarry solid was isolated by filtration.

Step 2) Purification of the coloured polymer:

The coloured polymer prepared in step 1) was dissolved in aqueous ammonia, precipitated by acidification with hydrochloric acid, isolated by filtration and washed with distilled water. This dissolving, isolation and precipitation process was then repeated again.

The coloured polymer was dissolved in aqueous ammonia and the solution was filtered through a cascade of filters (Glass microfibre (GF/A, GF/F and membrane)) to 0.45 micron and then purified by reverse osmosis using a 3000 MW cut off membrane and evaporated to dryness at approximately 70°C to give the coloured polymer having repeat units of Formula 8 (1.0g). The coloured polymer had a red shade with a λ_{max} of 507nm in water.



Formula 8

Coloured Polymers 2-7

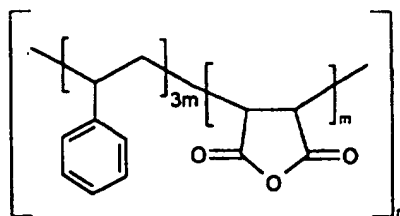
Coloured polymers were prepared using the general method described above for Coloured Polymer 1, except that the colorants and anhydride polymers shown below in Table 1 were used.

Table 1

Coloured Polymer	Colorant	Colorant	Polymer	Polymer	λ max
2	1	4.1 g	Polystyrene/maleic anhydride* (2:1 molar, Mn 1700)	2.92 g	406 nm
3	1	4.0 g	Polyethylene/maleic anhydride# (1:1 molar CAS No 9006-26-2)	3.0 g	461 nm
4	2	2.0 g	Polystyrene/maleic anhydride* (3:1 molar, Mn 1900)	4.05 g	460 nm
5	4	4.1 g	Polystyrene/maleic anhydride (2:1 molar, Mn 1700)	7.5 g	573 nm
6	5	3.0 g	Polystyrene/maleic anhydride (3:1 molar, Mn 1900)	2.05 g	627 nm
7	6	4.1 g	Polystyrene/maleic anhydride (2:1 molar, Mn 1700)	8.9 g	585 nm
* Available from Polysciences Inc.					
# Available from Sigma Chemical Co.					
λ max was measured in aqueous ammonia solution					

Coloured Polymer 8

- 5 A coloured polymer was prepared using a polymer carrying anhydride groups having repeat units of Formula 9, a bridging compound and a diazo mixture as shown below.



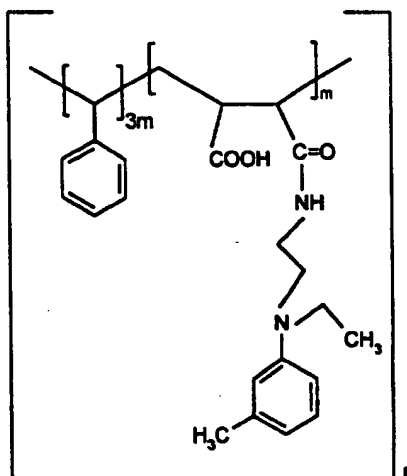
Formula 9

10

Step 1) Reaction of a polymer carrying anhydride group with a bridging compound.

- 15 N-ethyl-N- β -aminoethyl-m-toluidine (3.3g) was added over 5 minutes to a stirred solution of poly(styrene-co-maleic anhydride) (75% styrene, CAS no. 26762-29-8, Mn 1900, Aldrich) (7.4g) in THF (25cm³). The mixture was warmed to 30°C and stirred for 18 hours. The mixture was evaporated to dryness to give a polymer having a bridging compound (11.9 g) with repeat units of Formula 10, as a glassy solid.

Step 2) Preparation of a diazo mixture:

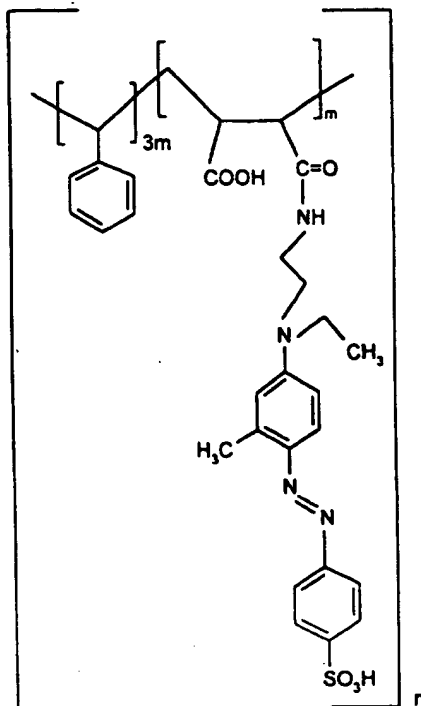


Formula 10

2N Sodium nitrite solution (6 cm³) was added to a stirred, cold (0-5°C) mixture of sulphanilic acid (1.7g), concentrated hydrochloric acid and water (50cm³). The mixture was stirred at 0-5°C for 1 hour and then an excess of sulphamic acid was added to destroy the remaining nitrous acid to give a diazo mixture.

Step 3) Preparation of the coloured polymer:

The diazo mixture prepared in step 2) was then added to a stirred, cooled (0-5°C) mixture of the polymer with a bridging compound (5.9g) prepared in step 1) in acetone (50cm³) over 15 minutes. The mixture was then allowed to warm up to room temperature and stirred for 18 hours. The pH was adjusted to about pH 6 by the addition of aqueous sodium acetate solution and a coloured polymer having repeat units of Formula 11 was isolated by filtration.



Formula 11

Step 4) Purification of the coloured polymer:

5 The coloured polymer prepared in step 3) was dissolved in aqueous ammonia at approximately pH 10, precipitated by acidification with hydrochloric acid, isolated by filtration and washed with distilled water. This dissolving, isolation and precipitation process was then repeated again.

10 The coloured polymer was dissolved in aqueous ammonia and the solution was filtered through a cascade of filters (Glass microfibre GF/A, GF/F and membrane) to 0.45 micron and then purified by reverse osmosis using a 1000 Mw cut off membrane and evaporated to dryness at approximately 70°C to give a yellow/orange coloured polymer (3.5g) having repeat units of Formula 11 with a λ max of 440 nm in aqueous ammonia solution.

15

Examples 1 to 6 Preparation of inks

15 Inks containing the number of parts of the coloured polymers from as specified in Table 2 below were then prepared in a stock solution of water (90 parts) and N-methylpyrrolidone (10 parts) with the addition of concentrated ammonia to give a pH of 9-10. The inks were then filtered through a 0.45 micron membrane filter and printed onto Gilbert Bond (GB) paper from Gilbert or Wiggins Conqueror (WC) paper using a Hewlett Packard 560 thermal ink jet printer. The properties of the resultant prints are shown in Table 2 below.

Table 2

Example	Coloured Polymer (parts) in ink	a = colour co-ordinates	b = colour co-ordinates	Optical density (OD)	Wet fastness (Run down /24 h)	Paper
1	1 (2.5)	+40.4	+12.5	0.984	3	GB
2	4 (2.5)	14.42	30.34	0.807	7	GB
3	8 (2.5)	30.45	52.40	1.033	9	GB
4	5 (2.5)	5.05	-4.82	0.855	10	GB
5	6 (5.0)	2.40	-36.67	0.724	10	WC
6	7 (5.0)	5.06	-8.68	1.234	9	GB

5 These prints were fast to both acidic and alkaline highlighter pens. The resultant prints had very good colour strength as indicated in Table 2 and showed very high wet fastness. Wet fastness is determined as follows: 0.5cm³ of water run down a test print only 5 minutes after printing produced virtually no stain on the white paper. (10 = no run down)

10 Colour co-ordinates and optical density were obtained using an X-rite spectrophotometer.

 The prints prepared from Example 1 lost 59% OD and the prints prepared in Example 3 lost 63% OD on fading for 100 hours in an accelerated light fastness test.

15 **Example 7:**

 Further inks may be prepared having the formulations described in Table 3 and Table 4 below wherein the following abbreviations are used. Water is included in each formulation to make the total number of parts up to 100. These inks may be applied to plain paper using an ink jet printer.

20

CP* : Identifies which of the coloured polymers (CP) may be used. The number of parts by weight of CP* is shown in brackets.

FRU : fructose

BZ : Benzyl alcohol

25 DEG : Diethylene glycol

DMB : Diethyleneglycol monobutyl ether

ACE : Acetone

IPA : Isopropyl alcohol

MEOH : Methanol

30 2P : 2-Pyrrolidone

MIBK : Methylisobutyl ketone

SUR : Surfinol 465 (a surfactant)

PHO : K_2PO_4

TEN : triethanolamine

NMP : N-methylpyrrolidone

5 TDG : Thiodiglycol

CAP : Caprolactam

BUT : Butylcellosolve

GLY : Glycerol

10

Table 3

CP* (parts)	BZ	DEG	ACE	NaOH	$(NH_4)_2SO_4$	IPA	MEOH	2P	MIBK
1 (5)	5		3				1		
4 (5)		3	2	0.3		4	3	15	9
3 (4)	4	-	1	0.2	-	3	1	-	-
1 (6)		2	2		0.4				
2 (8)	-	10	2	0.2	-	-	-	-	5
4 (5)	1	4	-	-	0.1	-	-	5	-
1 (10)	8	9					2	9	1
1 (4)		3	3	0.4		5	4	6	1
1 (10)	10				0.5	8			4
5 (11)	-	3	-	0.1	-	4	2	-	3
4 (5)	15	1	1	0.2				15	
6 (5)	3	-	2	-	0.2	-	8	-	4
7 (12)	4	1	1	0.1	-	1	-	1	2
8 (6)	3	-	-	-	0.3	10	1	3	-
3 (17)	4		4						3
2 (4)	5	2		0.1	0.1	5	4	8	
1 (3)	6		6						5
4 (10)	7	3						10	3
2 (3)	5		1		0.2	3	2		
1 (7)		2	5			2		10	6
2 (4)	8	1	7	0.4				13	
1 (7)	5	1	1		0.1	8		14	2

(Water is included in each formulation to make the total number of parts up to 100)

Table 4

CP* (parts)	BZ	NMP	SUR	TEN	TDG	FRU	PHO	DMB
1 (10)	3	-	0.1	-	-	0.1	-	3
1 (15)	6	15	-	-	20	-	0.2	-
8 (10)	1	-	0.2	0.5	-	0.5	-	5
3 (10)	4	10	-	-	5	-	-	2
1 (5)	10	20	-	-	10	-	-	-
9 (15)	-	-	-	-	-	1	0.3	-
4 (8)	2	10	0.1	-	-	1	0.5	-
5 (10)	10	4	-	0.2	5	2	-	-
5 (12)	-	20	0.2	0.2	-	2	-	-
1 (10)	-	-	-	-	-	-	-	4
1 (15)	9	15	-	-	-	-	-	-
6 (20)	10	-	0.3	-	8	3	-	1
4 (10)	5	-	0.3	0.5	15	-	1	6
7 (15)	-	17	-	0.1	3	-	1	10
8 (11)	5	-	-	0.1	-	-	-	5
4 (12)	5	17	-	-	-	0.5	-	4
1 (15)	10	5	0.1	0.2	2	-	-	5
1 (10)	8	-	-	-	12	-	0.2	-
3 (20)	-	10	-	-	-	2	-	5
2 (13)	-	2	-	-	-	0.5	-	
5 (5)	-	12	0.1	-	-	0.5	-	1
1 (5)	9	-	-	1	1	-	0.1	10

(Water is included in each formulation to make the total number of parts up to 100)

CLAIMS

1. An ink having an viscosity less than 20cp at 20°C comprising the components:
(a) a coloured polymer obtainable by the coloration of a polymer carrying anhydride
5 groups; and
(b) a liquid medium.
2. An ink according to claim 1 wherein coloration of a polymer carrying anhydride
groups comprises the formation of a covalent bond between the polymer and a colorant.
10
3. An ink according to claim 1 wherein coloration of the polymer carrying anhydride
groups comprises reaction of the anhydride groups with a colorant precursor thereby
forming a covalent bond therebetween and subsequently converting the colorant
precursor to a colorant.
15
4. An ink according to claim 1 wherein coloration of the polymer carrying anhydride
groups comprises the reaction of the anhydride groups with a bridging compound
thereby forming a covalent bond therebetween and subsequently reacting the bridging
group with a colorant or colorant precursor.
20
5. An ink according to claim 2 wherein the covalent bond is formed by the reaction
of nucleophilic group(s) on the colorant with the anhydride groups of the polymer.
6. An ink according to claim 3 wherein the covalent bond is formed between the
25 polymer having anhydride groups and the colorant precursor by the reaction of
nucleophilic group(s) on the colorant precursor with anhydride groups in the polymer.
7. An ink according to claim 4 wherein the covalent bond is formed between the
polymer having anhydride groups and the bridging compound by the reaction of
30 nucleophilic group(s) on the bridging compound with anhydride groups in the polymer.
8. An ink according to claims 5,6 or 7 wherein the nucleophilic group(s) are
selected from hydroxy, thio and amine groups.
9. An ink according to claims 3 or 4 wherein the colorant precursor is converted to
35 the coloured compound by a process comprising a diazotisation reaction.

10. An ink according to claim 9 wherein the diazotisation reaction comprises the steps:

- (i) diazotising an amino group in the colorant precursor using a diazotising agent; and
- 5 (ii) coupling the product of step (i) with a coupling component forming an azo group therebetween.

11. An ink according to any one of the preceding claims wherein the polymer carrying anhydride groups has a weight average molecular weight less than 70,000.

10

12. An ink according to any one of the preceding claims wherein the coloured polymer is completely dissipated in the liquid medium.

15

13. An ink according to any one of the preceding claims wherein the liquid medium comprises water and an organic solvent.

14. An ink according to any one of the preceding claims wherein the polymer carrying anhydride groups is obtainable from the polymerisation of maleic anhydride monomers.

20

15. An ink according to any one of the preceding claims wherein the polymer carrying anhydride groups is a copolymer.

25

16. An ink according to any one of the preceding claims wherein the liquid medium comprises a mixture of water and an organic solvent, wherein the weight ratio of water to organic solvent is from 99:1 to 1:99.

30

17. An ink according to any one of the preceding claims which comprises from 0.25 to 30 parts of component (a) and from 70 to 99.75 parts of component (b), wherein all parts are by weight and the number of parts of (a) + (b) = 100.

35

18. An ink according to any one of the preceding claims for use in an ink jet printer.

19. A process for forming an image on a substrate comprising applying thereto an ink using an ink jet printer, characterised in that the ink is as defined in any one of claims 1 to 17.

20. A paper or an overhead projector slide printed with an ink as defined in any one of claims 1 to 17.

21. An ink jet printer cartridge, optionally refillable, containing an ink as defined in any one of claims 1 to 17.

22. Inks substantially as described in examples 1 to 7.



Application No: GB 9929231.0
Claims searched: 1-22

Examiner: Dr Albert Mthupha
Date of search: 29 March 2000

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R): C3V (VAD, VAR)

Int Cl (Ed.7): C09D (11/00, 11/02, 11/10)

Other: ONLINE: EPODOC, JAPIO, WPI.

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	US 3903034 A DICK, see column 2 lines 25-37, column 3 lines 44-48 & Examples 1-4, 6, 8.	1, 12, 14-15, 18-20 at least.
X	US 3687887 A DICK, see column 4 lines 3-9 & Example 2.	1, 12, 14-15, 18-20 at least.
X	WPI Abstract AN 1999-076650 [07] & JP 100316907 A (INCTEC), see Abstract.	1, 12, 14-15, 18-20 at least.

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.